

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) **EP 1 037 112 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
20.09.2000 Bulletin 2000/38

(51) Int. Cl.⁷: **G03F 7/039**, G03F 7/037,
G03F 7/022, C08L 79/08

(21) Application number: **99940701.8**

(86) International application number:
PCT/JP99/04849

(22) Date of filing: **07.09.1999**

(87) International publication number:
WO 00/14604 (16.03.2000 Gazette 2000/11)

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

(30) Priority: **09.09.1998 JP 25535698**
13.10.1998 JP 29048198
06.11.1998 JP 31599098

(71) Applicant:
TORAY INDUSTRIES, INC.
Tokyo 103-8666 (JP)

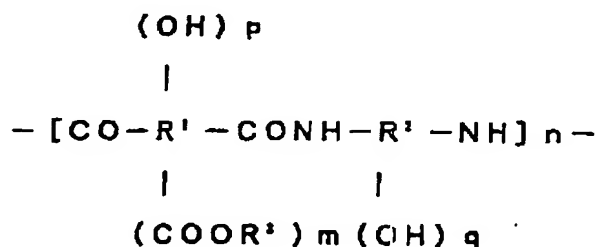
(72) Inventors:
• **TOMIKAWA, Masao**
Otsu-shi, Shiga 520-0865 (JP)

• **OKAMOTO, Naoyo**
Nagoya-shi, Aichi 462-0846 (JP)
• **YOSHIDA, Satoshi**
Otsu-shi, Shiga 520-0842 (JP)
• **OKUDA, Ryoji**
Otsu-shi, Shiga 520-0842 (JP)

(74) Representative:
Coleiro, Raymond et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(54) **POSITIVE PHOTSENSITIVE RESIN PRECURSOR COMPOSITION AND PROCESS FOR PRODUCING THE SAME**

(57) The present invention relates to a positive-working photosensitive resin precursor composition which is characterized in that it contains (a) polymer in which the chief component comprises structural units of the kind where the bonding between structural units is represented by general formula (1) and (b) photoacid generator, and it can form a pattern by light irradiation and subsequent developing, and the total carboxyl groups contained in said polymer is from 0.02 to 2.0 mmol/g, and it provides a photosensitive resin composition of high sensitivity which can be developed by alkali.



(R¹ is an organic group of valency from 3 to 8 having at least 2 carbon atoms, R² is an organic group of valency from 2 to 6 having at least 2 carbon atoms, R³ is hydrogen or an organic group with from 1 to 20 carbons. n is an integer of value from 3 to 100,000, m is 1 or 2, p and q are integers of value from 0 to 4 and p + q > 0.)

EP 1 037 112 A1

Description

Technical Field

- 5 **[0001]** The present invention relates to a photosensitive resin composition which can be used for the interlayer dielectrics of semiconductor devices and for buffer coat films, α -ray shielding films and the like, and which can form patterns by exposing to actinic radiation and dissolving away the exposed regions with aqueous alkali solution.

Technical Background

- 10 **[0002]** Heat-resistant resins such as polyimides are employed in the semiconductor field to form interlayer dielectrics, buffer coat films, α -ray shielding films and the like. In using a polyimide in such applications, patterning of the polyimide film is necessary for the purpose of through hole formation and the like. For example, a solution of the polyamic acid, which is the polyimide precursor, is applied to the substrate, and then converted to the polyimide by heat treatment, after which a positive photoresist relief pattern is formed on the polyimide film and, with this as a mask, patterning is carried out by selective etching of the polyimide film by means of a hydrazine etching agent. However, this method has the problem that, as well as the process being complex since it includes the photoresist application and removal steps, etc., dimensional accuracy is lowered because of side etching. For such reasons, photosensitive resin compositions have been investigated which are heat-resistant resins, or precursors which can be converted to heat-resistant resins by means of a heat treatment or the like, and which themselves can undergo pattern processing.

- 15 **[0003]** For photosensitive resin compositions to have a pattern accuracy enabling them to be employed in passivation layer pattern formation, a method has been investigated whereby first of all patterning and curing of the photosensitive resin precursor composition is carried out on the passivation layer prior to pattern formation and then, with this pattern as a mask, dry etching of the underlying passivation layer is carried out (the one mask process). In accordance with this method, it is possible to shorten the process required in passivation layer pattern formation, leading to a reduction in costs.

- 20 **[0004]** When using a photosensitive resin composition, normally application and drying on the substrate are performed in the solution state, and irradiation with active light rays is performed through a mask. As negative-working photosensitive resin precursor compositions where the exposed regions are left following the developing, there are known compositions where a carbon-carbon double bond which is dimerized or polymerized by actinic radiation and an amino group or quaternized salt thereof are added to a polyamic acid (JP-B-59-52822), compositions where an acrylamide is added to the polyamic acid (JP-A-3-170555) and compositions where a polyimide precursor with a carbon-carbon double bond, a specified oxime compound and a sensitising agent are incorporated (JP-A-61-118423). However, there is the problem that changing over from a conventional non photosensitive resin composition patterning process using a positive-working photoresist to a process using a negative-working photosensitive resin composition requires a change in the exposure device mask and a change in the developing equipment. Furthermore, these negative-working photosensitive resin compositions employ organic solvents in the developing, but from the point of view of preventing environmental pollution and improving the working environment, a photosensitive material which can be developed with an aqueous developer liquid instead of an organic developer liquid is desirable. For these reasons, alkali-developable positive-working photosensitive resin compositions are being investigated.

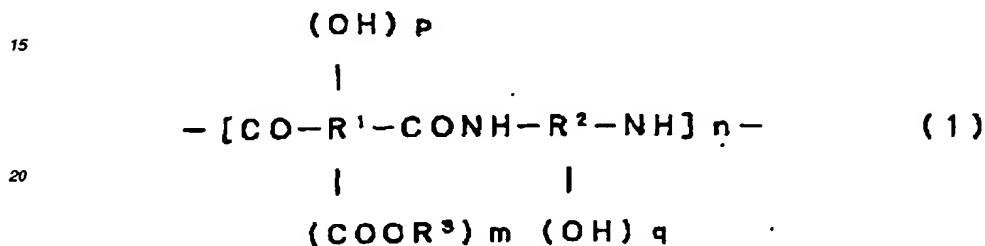
- 25 **[0005]** As known examples of positive-working photosensitive resin compositions where the exposed regions are dissolved away by developing with an aqueous alkali solution, there are the polyimide precursors where o-nitrobenzyl groups have been introduced by ester bonds (JP-A-60-37550), the composition where an o-quinone diazide compound is mixed into a polyamic acid ester (JP-A-2-181149), the composition where an o-quinone diazide compound is mixed with a polyamic acid or polyamic acid ester which has a phenolic hydroxyl group (JP-A-3-115461), the composition where an o-quinone diazide compound is mixed with a polyimide which has a phenolic hydroxyl group (JP-3-177455), and the composition where an o-quinone diazide compound is mixed with a polyhydroxyamide (JP-B-1-46862).

- 30 **[0006]** However, the polyimide precursors with o-nitrobenzyl groups introduced by means of ester bonds have the problem that the sensitising wavelengths are mainly below 300 nm and the sensitivity is low. In the case where an o-quinone diazide compound is mixed into the polyamic acid ester, the rate of dissolution by the alkali developer is low, so the sensitivity is low and the developing time is lengthy. In the case where an o-quinone diazide compound is added to a polyamic acid with a phenolic hydroxyl group, the solubility in the alkali developer is too great, so there is the problem that only dilute developer liquid can be employed and, since the unexposed regions are swollen by the developer liquid, fine patterning is difficult. Where an o-quinone diazide compound is mixed with a polyamic acid compound or polyimide with a phenolic hydroxyl group, the dissolution rate in the alkali developer is improved but there is the problem that further adjustment of the dissolution rate is difficult. Where an o-quinone diazide compound is mixed with a polyhydroxyamide, the dissolution rate in the alkali developer is improved but there is the problem that change to the polymer composition is required for further adjustment in the dissolution rate. The present invention has been made in view

of these various problems of the prior art, and it has as its objective to offer a photosensitive resin composition where adjustment of the dissolution time in the aqueous alkali solution is possible and, furthermore, where the polymer transparency is high at the exposure wavelengths and which has high sensitivity.

5 Disclosure of the Invention

[0007] The present invention is a positive-working photosensitive resin composition which is characterized in that it contains (a) polymer in which the chief component comprises structural units of the kind where the bonding between structural units is represented by general formula (1) and (b) photoacid generator, and which can form a pattern by light irradiation and subsequent developing, and the total carboxyl groups contained in 1 g of said polymer is from 0.02 to 2.0 mmol.

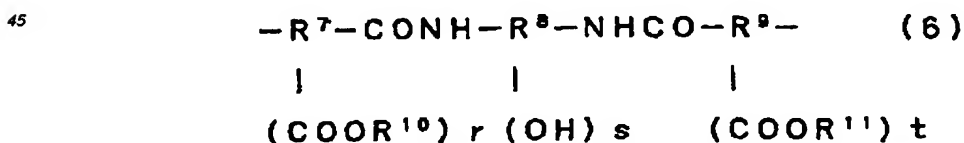


(R¹ is an organic group of valency from 3 to 8 having at least 2 carbon atoms, R² is an organic group of valency from 2 to 6 having at least 2 carbon atoms, R³ is hydrogen or an organic group with from 1 to 20 carbons but it is not all hydrogen. n is an integer of value from 3 to 100,000, m is 1 or 2, p and q are integers of value from 0 to 4 and p + q > 0.)

30 Optimum Form for Practising the Invention

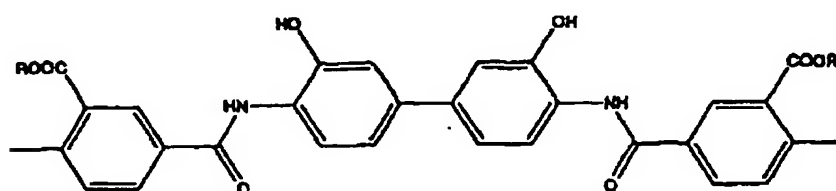
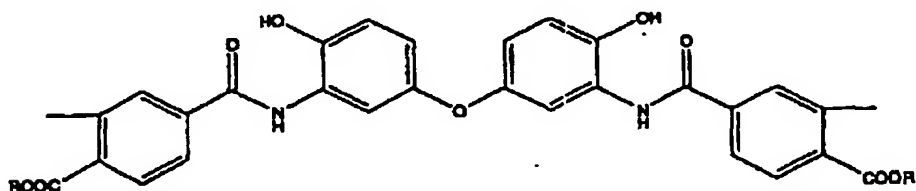
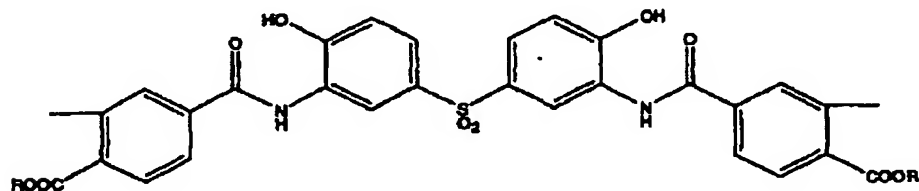
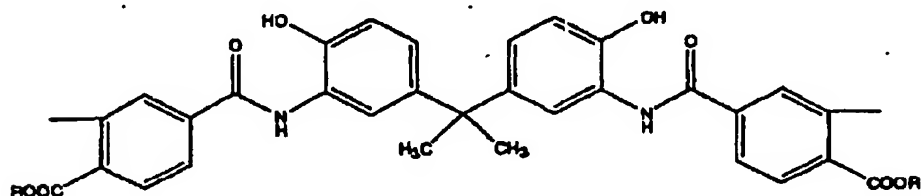
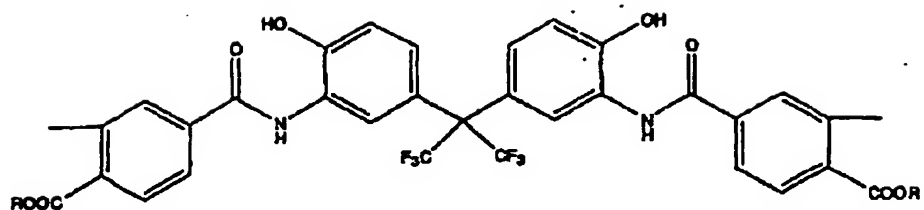
[0008] In the present invention, the polymer represented by general formula (1) is preferably one which can form a polymer with imide rings, oxazole rings or other cyclic structures by heating or by means of a suitable catalyst. By forming cyclic structures, the heat resistance and solvent resistance are markedly enhanced. The polymer in which structural units represented by aforesaid general formula (1) are the chief component preferably has hydroxyl groups. In such circumstances, because of the presence of the hydroxyl groups, the solubility in aqueous alkali solution is better than that of a polyamic acid which does not have hydroxyl groups. In particular, from amongst hydroxyl groups, phenolic hydroxyl groups are preferred in terms of their solubility in aqueous alkali solution.

[0009] The residual group which constitutes R¹ in general formula (1) denotes an acid structural component, and this acid component is preferably a C₂ to C₆₀ trivalent to octavalent group containing an aromatic ring and having from one to four hydroxyl groups. Where R¹ does not contain hydroxyl groups, desirably the R² component contains from one to four hydroxyl groups. An example is shown by general formula (6).



(R⁷ and R⁹ represent C₂ to C₂₀ organic groups of valency 3 or 4, R⁸ represents a hydroxyl group-containing C₃ to C₂₀ organic group of valency from 3 to 6, and R¹⁰ and R¹¹ are each hydrogen or a C₁ to C₁₀ monovalent organic group. R¹⁰ and R¹¹ are not all hydrogen atoms, nor are they all C₁ to C₁₀ monovalent organic groups. r and t represent the integers 1 or 2, and s denotes an integer of value from 1 to 4.)

[0010] Furthermore, the hydroxyl groups are preferably in a position adjacent to an amide bond. As examples thereof, there are structures of the kind shown in (10) below, but the present invention is not restricted to these.



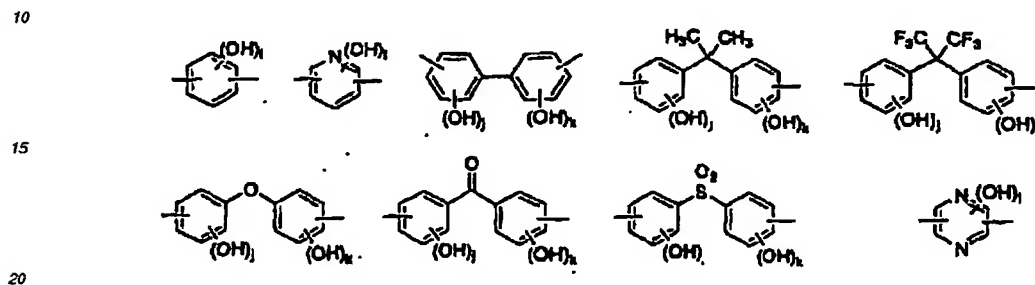
(10)

(R is a hydrogen atom or a C₁ to C₂₀ monovalent organic group)

[0011] Furthermore, for the residual groups containing R¹, it is also possible to employ tetracarboxylic acids, tricarboxylic acids and dicarboxylic acids which do not contain hydroxyl groups. As examples thereof, there are aromatic tetracarboxylic acids such as pyromellitic acid, benzophenonetetracarboxylic acid, biphenyltetracarboxylic acid, diphenyl ether tetracarboxylic acid and diphenyl sulphone tetracarboxylic acid, and the diesters thereof where two of the carboxyl groups are in the methyl or ethyl group form; aliphatic tetracarboxylic acids such as butane tetracarboxylic acid and cyclopentane tetracarboxylic acid, and the diesters thereof where two of the carboxyl groups are in the methyl or ethyl group form; and aromatic tricarboxylic acids such as trimellitic acid, trimesic acid, naphthalene tricarboxylic acid and the like.

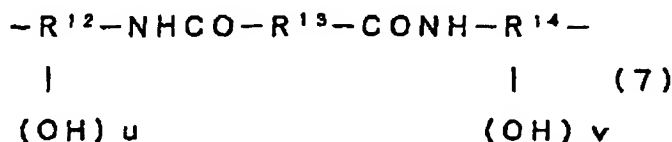
[0012] The residual group which constitutes R^2 in general formula (1) denotes a diamine structural component. Preferred examples of R^2 are those with an aromatic ring, from the point of view of the heat resistance of the polymer obtained, and also having from one to four hydroxyl groups. Where R^2 does not have hydroxyl groups, it is desirable that the R^1 component contain from one to four hydroxyl groups. Furthermore, the hydroxyl groups are preferably positioned adjacent to an amide bond.

[0013] As specific examples, there are compounds such as bis(aminohydroxyphenyl)hexafluoropropane, diamino-dihydroxypyrimidine, diaminodihydroxypyridine, hydroxydiaminopyrimidine, diaminophenol and dihydroxybenzene, and those with the following structures.

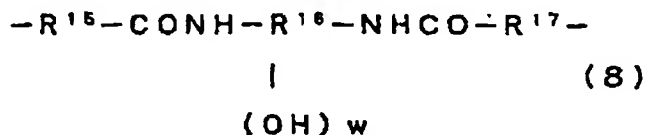


(i is an integer in the range 1 to 4, j and k are integers in the range 0 to 4, and j + k is at least 1.)

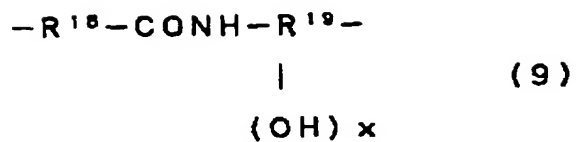
[0014] Amongst these R^2 components, as further preferred examples there can be cited the compounds with the structures shown by general formulae (7), (8) and (9). Of these, specific examples of further preferred structures are exemplified by general formulae (11), (12) and (13).



(R^{12} and R^{14} represent hydroxyl group-containing C_2 to C_{20} organic groups of valency 3 or 4, and R^{13} represents a C_2 to C_{30} divalent organic group. u and v represent the integers 1 or 2.)

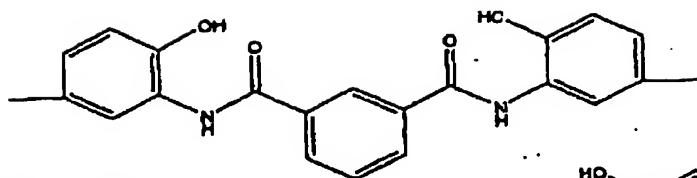


(R^{15} and R^{17} represent C_2 to C_{30} divalent organic groups, and R^{16} represents a hydroxyl group-containing C_2 to C_{20} organic group of valency 3 to 6. w represents an integer in the range 1 to 4.)

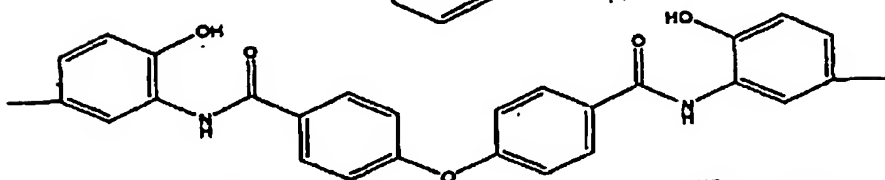


(R¹⁸ represents a C₂ to C₃₀ divalent organic group, and R¹⁹ represents a hydroxyl group-containing C₂ to C₂₀ organic group of valency 3 to 6. x represents an integer in the range 1 to 4.)

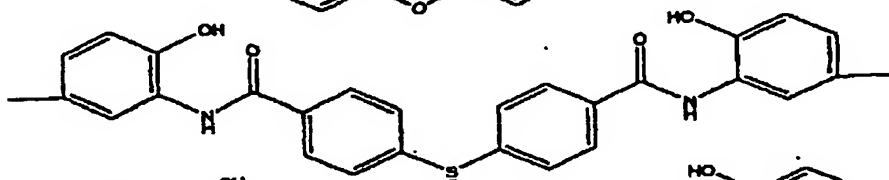
5



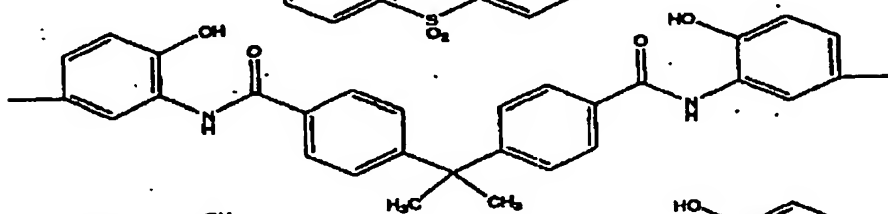
10



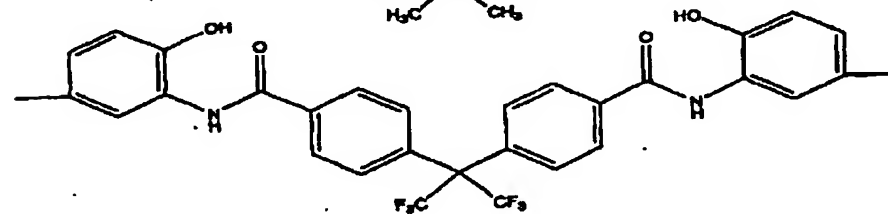
15



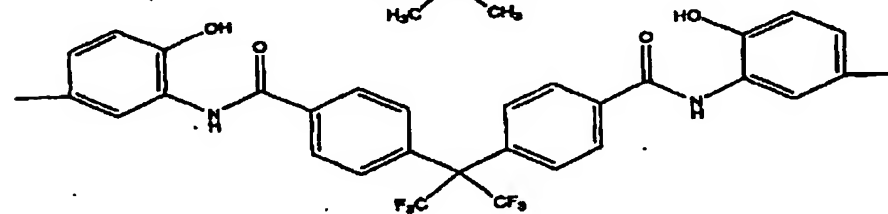
20



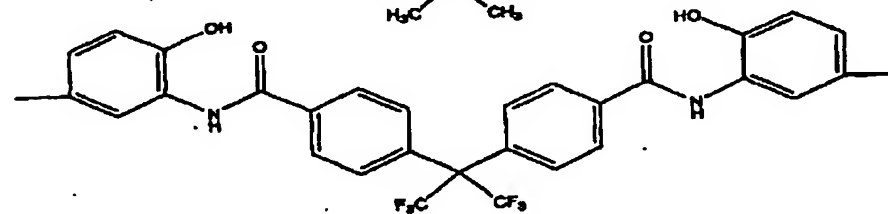
25



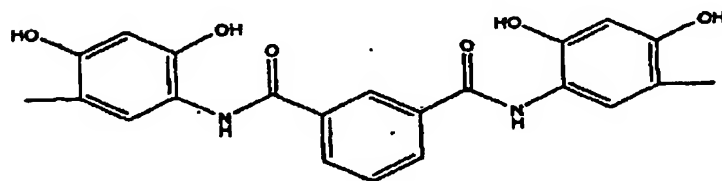
30



35



40

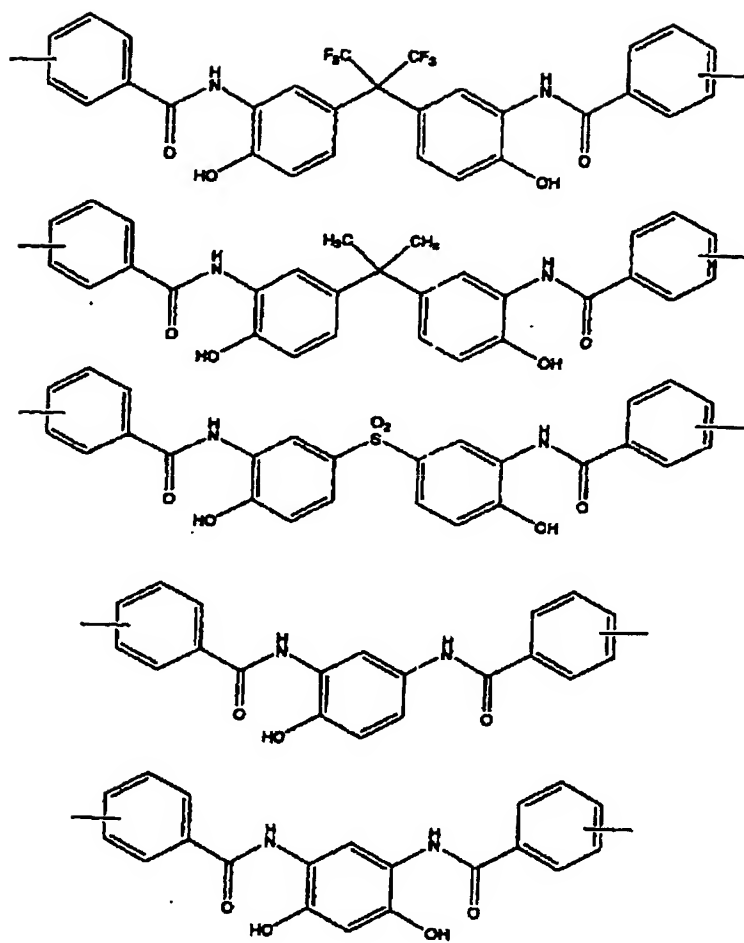


45

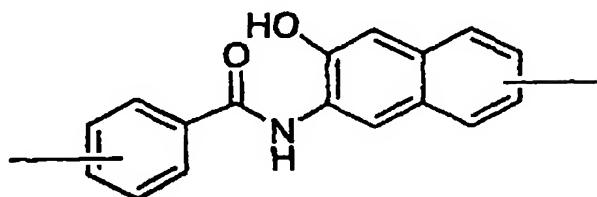
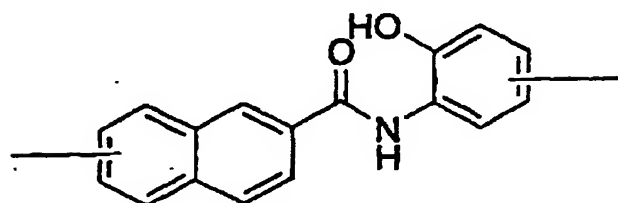
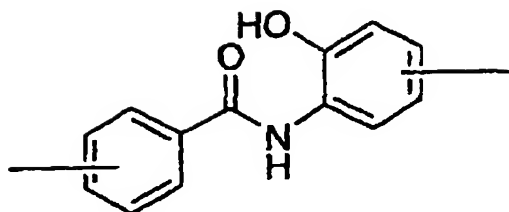
(1 1)

50

55



(1 2)



(1 3)

[0015] Furthermore, it is also possible to use a diamine which does not contain a hydroxyl group for the residual group containing R^2 in general formula (1). As examples thereof, there are phenylenediamine, diaminodiphenyl ether, aminophenoxybenzene, diaminodiphenylmethane, diaminodiphenylsulphone, bis(trifluoromethyl)benzidine, bis(aminophenoxyphenyl)propane, bis(aminophenoxyphenyl)sulphone or compounds comprising these aromatic rings with alkyl group and/or halogen atom substituents, and aliphatic cyclohexyldiamine, methylene biscyclohexylamine and the like. These diamine compounds can be used on their own or they can be used in combinations of two or more types. It is preferred that they be used as no more than 40 mol% of the diamine component. If more than 40 mol% is copolymerized then the heat resistance of the polymer obtained is lowered.

[0016] With the objective of improving the adhesion to the substrate, it is also possible to use a diamine compound with a siloxane structure within a range such that the heat resistance is not lowered. As examples of diamines with a siloxane structure, there may be used bis(3-aminopropyl)tetramethyldisiloxane, bis(3-aminopropyl)tetraphenyldisiloxane, bis(4-aminophenyl)tetramethyldisiloxane and the like.

[0017] R^3 in general formula (1) represents hydrogen or a C_1 to C_{20} organic group. If the number of carbons in R^3 exceeds 20 then the solubility in aqueous alkali is lost. In terms of the stability of the photosensitive resin solution obtained, R^3 is preferably an organic group, but hydrogen is preferred in terms of the solubility in aqueous alkali. In other words, it is not desirable that R^3 all be hydrogen or that it all be an organic group. By adjusting the proportion of R^3 which comprises hydrogen or which comprises an organic group, the dissolution rate in aqueous alkali solution may be varied, so by such adjustment it is possible to obtain a photosensitive resin composition with a suitable dissolution rate.